Journal of Physics: Conference Series

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Abstract. Structural features, magnetic properties and magnetocaloric effect of pure Gd ribbons prepared by melt spinning method were carefully analyzed. The X-ray data show that there is no change in the cell parameters for the samples prepared at different copper-wheel speed. Average size of nanocrystalline grains was close to 30 nm. As compared to the bulk Gd sample, the Curie temperature was the same in the case of the ribbons. From the magnetic isotherms, the magnetic entropy change was derived using the Maxwell relation follow the standard procedure. Its value was comparable with the value of the bulk Gd. Good mechanical properties of fabricated Gd ribbon and their flexibility can be useful for design of flexible refrigerating elements.

1. Introduction

The great interest in the study of the magnetocaloric effect (MCE) is understandable in a view of prediction that refrigerators operating on the basis of magnetocaloric effect will be more energy efficient than modern refrigerators based on compression and expansion of gases. At the moment great efforts are focused on finding new functional materials for such devices including MCE materials for flexible devices [1, 2]. Nevertheless, despite some progress in this direction, gadolinium remains the most effective functional material for magnetic refrigerators operating near room temperature [3]. However, the methods of preparation and the shape of the refrigerating elements can be very different: bulk pieces [4], nanocrystalline ribbons [5, 6], foils [3, 7], thin films and multilayered structures [8-13]. Among them, nanocrystalline ribbons have certain advantages. Firstly, they can be produced by well-known melt-spinning technique, which is characterized by high performance, relative ease of use, the possibility of varying the operating parameters and large production rate [14]. Secondly, the ribbons have a large surface (both sides are involved in the heat transfer), which contributes to the effective heat transportation and refrigeration [15, 16]. At the same time, there are only very limited data in the literature regarding the properties of pure gadolinium ribbons, prepared by melt spinning [5, 6, 17]. However, it is not always possible to accurately predict the properties of such materials in advance, since the rapid quenching technique itself allows the formation of non-equilibrium structures [14].

Journal of Physics: Conference Series **1389** (2019) 012100 doi:10.1088/1742-6596/1389/1/012100

In this work, we present a detailed study on the structural peculiarities, magnetic properties and magnetocaloric effect of Gd ribbons prepared in different conditions by melt spinning in a purified argon atmosphere.

2. Experimental

Gadolinium (Gd of 99.96% purity) rapidly quenched ribbons were prepared using a laboratory scale single roller melt-spinning device operating in a purified argon atmosphere. A free jet of liquid metal was ejected from a circular nozzle. A Cu-wheel speed (s_w) was as high as 20 m/s to 45 m/s and speed of the crucible scanning on the surface of the copper wheel was as high as 7×10^{-4} m/s. The structure of ribbons was studied by X-ray diffraction (XRD) using a PHILIPS X'PERT PRO automatic diffractometer operating with Cu-Ka radiation (wave length $\lambda = 1.54$ Å). The magnetic properties of the samples were measured by a Quantum Design SQUID magnetometer (MPMS XL7) and vibrating sample magnetometer (Lake Shore Cryotronics). The magnetic entropy change $\Delta S_M(H, T)$ was quantified using the Maxwell relation follow the standard procedure.

3. Results and discussion

Obtained samples were long rectangular pieces with large length of tens cm and width of about few mm. Increasing the Cu-wheel speed from 20 m/s to 45 m/s leads to a decrease in the width of the ribbon from 3 mm to 1.5 mm, while the thickness of the belt decreases from 70 to 40 µm. All kinds of the ribbons had very good mechanical properties and allowed mechanical processing. However, a change in the geometric parameters of the ribbons obtained at different regimes of Cu-wheel speed did not affect the features of their structural state. XRD experimental data were in good agreement meanly with a Gadolinium hexagonal structure (04-019-0727 data base file), the positions at 28.73° and 31.09° in 2θ for the intense reflections (100) and (002) respectively were used to calculate the starting unit cell parameters 3.585 Å and 5.750 Å, for "a" and "c" parameters, respectively. Figure 1 shows X-ray diffraction pattern for Gd ribbon prepared at s_w of 20 m/s as an example. The average size of the crystalline domains (coherently diffracting domain volumes) of the sample was extracted from the broadening of the signal using the Scherrer equation. The obtained results show crystal sizes near 30 nm for all the analyzed samples.

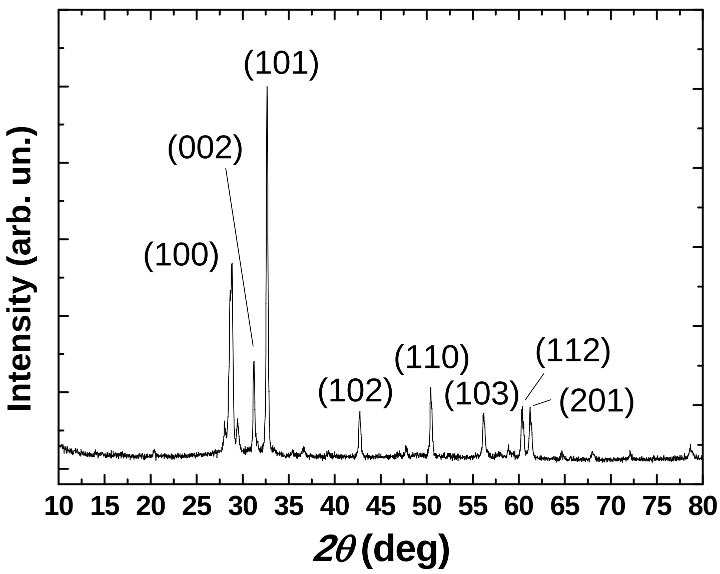

Figure 1. X-ray diffraction measurement results for the Gd melt-spun ribbon prepared at s_w of 20 m/s.

Figure 2 shows the temperature dependence of the magnetization, $M(T)$, for Gd ribbons prepared at s_w of 20 and 45 m/s as an example. The Curie temperature, T_C = 294 K, was estimated from the magnetization on temperature dependence $M(T)$ as the minimum of the dM/dT versus T variation (see inset). Very narrow minimum corresponding to $dM/dT(T)$ confirms the high homogeneity of the fabricated ribbons. It is clearly seen that the T_C value does not depend on the s_w parameter and it is the same as T_C value for bulk Gd. Figure 3 shows magnetic hysteresis loops measured at T = 5 K. It is seen that the saturation magnetization M_s of two samples are very close to each other in frame of the experimental errors values. Obtained M_s value was below of the M_s of the bulk gadolinium by the 6% only.

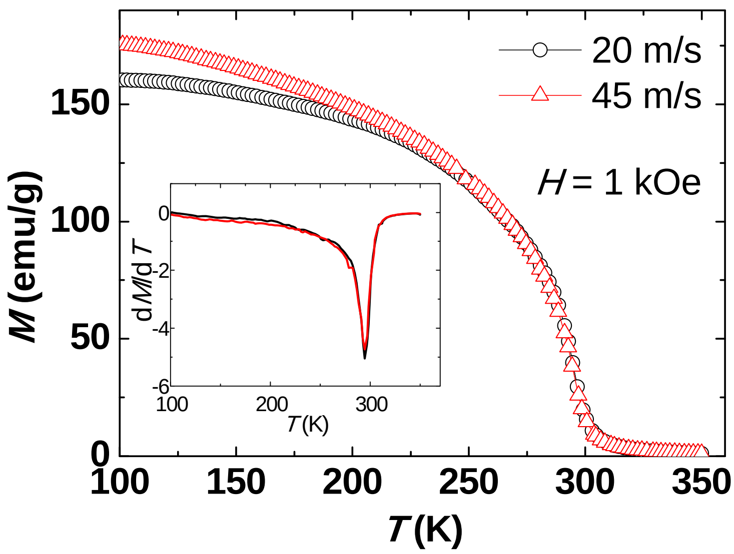

Figure 2. Temperature dependence of magnetization for Gd ribbons prepared at s_w of 20 and 45 m/s. Inset: the dM/dT versus T curves.

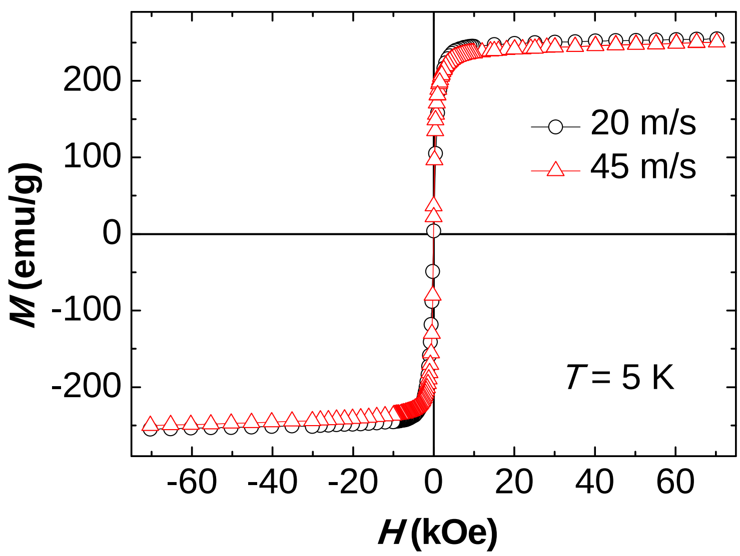

Figure 3. Hysteresis loops measured at T = 5 K for Gd ribbons prepared at s_w of 20 and 45 m/s.

The MCE value was calculated as the change in magnetic entropy using big number of magnetic isotherms measured in a wide temperature range below and above the temperature of the magnetic ordering of the sample. Magnetic isotherm curves were measured in increments of 5 degrees. The magnetic field was applied in the plane of the ribbon samples and increased up to 17 kOe. Such a value of the maximum measuring field was selected taking into account that the magnetic fields of the order of 10–20 kOe can be created by modern permanent magnets [18]. For the temperature range $T < T_C$, the magnetization value shows intensive growth in small magnetic fields, and afterwards a tendency of saturation in the large fields is observed. This is a behavior typical for ferromagnetic materials. In the interval of higher temperatures $T > T_C$, the shape of the $M(H)$ curves become close to a linear one. This is a behaviour typical for paramagnetic materials (Fig. 4).

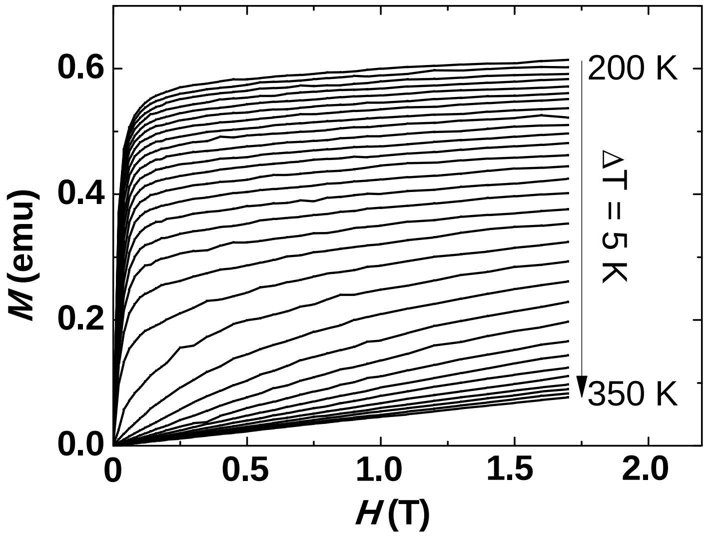

Figure 4. Magnetization isotherms of the Gd ribbon prepared at s_w = 20 m/s.

To understand the origin of the magnetic phase transition in the fabricated ribbons, the measured *M–H* isotherms were converted to M^2 versus H/M plots (so-called Belov-Arrott plots) (Fig. 5). Application of the Banerjee criterion [19] allows to make following comments: the positive or negative slope of M^2 versus H/M curves allows to distinguish between the magnetic phase transition of the second or the first order. In the present case, slopes of all curves are positive (Fig. 5), indicating that around Curie temperature a second-order magnetic phase transition from ferromagnetism to paramagnetism takes place. In addition, the extrapolation of Belov-Arrott curves confirmed that for this sample T_C = 294 K.

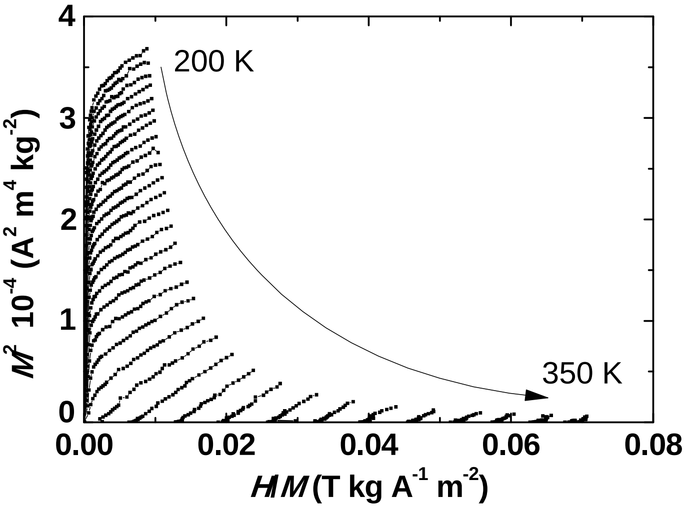

Figure 5. Isothermal M^2 versus H/M plots of the Gd ribbon prepared at s_w = 20 m/s.

The change in magnetic entropy was determined through magnetic isotherms using the Maxwell ratio [20]:

$$\Delta S_M = \int_{H_2}^{H_1} \left(\frac{\partial M}{\partial T} \right)_H dH \tag{1}$$

where ΔS_M – change in magnetic entropy, H - magnetic field, M - magnetization, T - temperature. The maximum of the ΔS_M value in the temperature dependence of the change in magnetic entropy turned out to be 4.8 J/kg·K at ΔH = 17 kOe (Fig. 6), which is very close to the corresponding value for the bulk gadolinium [3, 21].

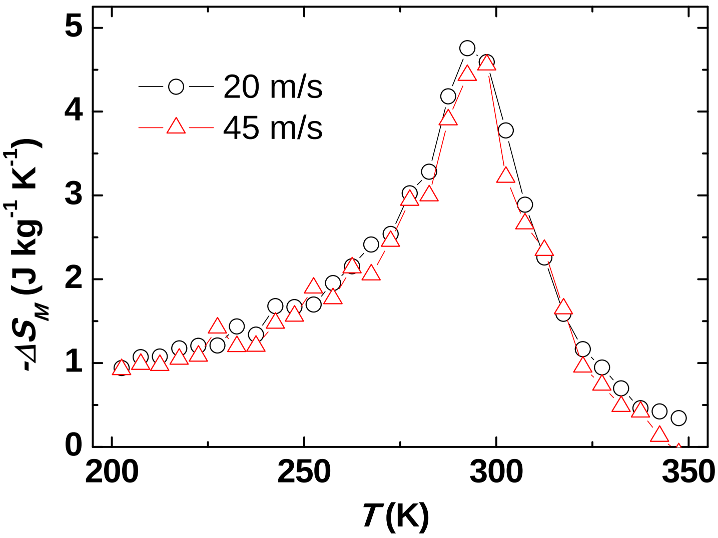

Figure 6. Temperature dependence of magnetic entropy change ($-\Delta S_M$) for Gd ribbons prepared at s_w of 20 and 45 m/s. ΔH = 17 kOe.

Based on the analysis of the magnetization curves and M^2 versus H/M plots (Figs. 7 and 8) similar conclusions can be made for Gd ribbon prepared at s_w = 45 m/s. $\Delta S_M(T)$ dependence features and ΔS_M peak values were very close to the parameters obtained in the case of Gd ribbons prepared at s_w = 20 m/s (Fig. 6).

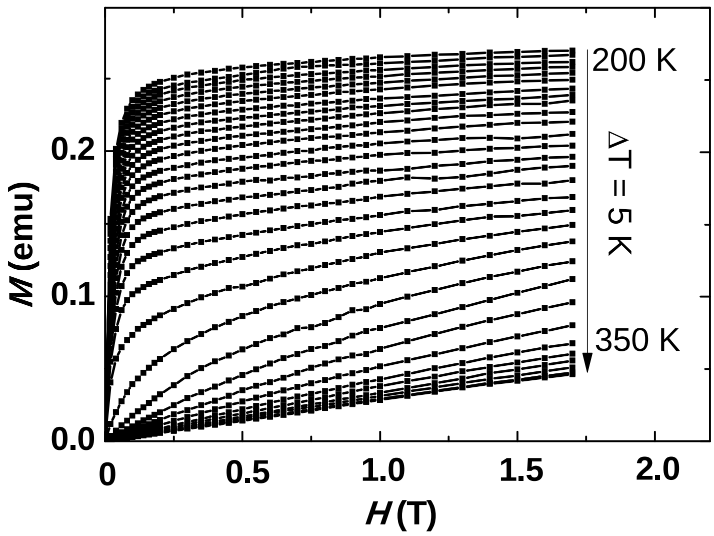

Figure 7. Magnetization isotherms of the Gd ribbon prepared at s_w = 45 m/s.

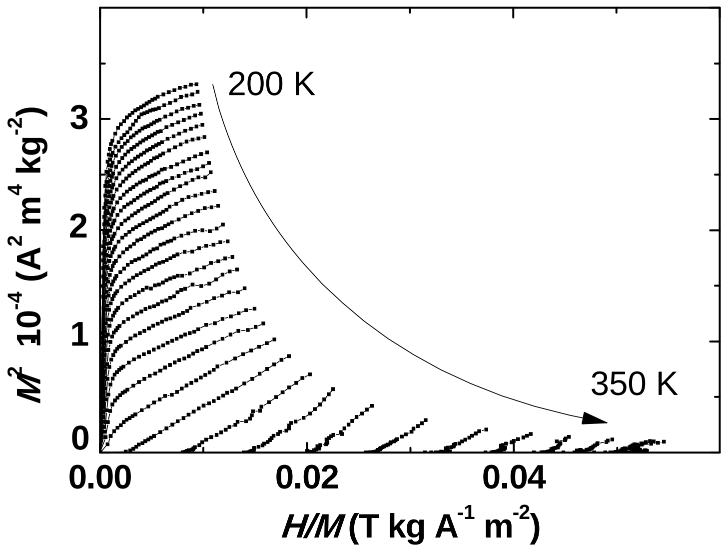

Figure 8. Isothermal M^2 versus H/M plots of the Gd ribbon prepared at s_w = 45 m/s.

Thus, Gd nanocrystalline ribbons possessing the same MCE effect value as bulk gadolinium can be prepared directly by melt spinning without any additional processing. The melt-spinning technique allows to obtain ribbons with the same value of magnetocaloric effect in a relatively wide range of s_w. However, the variation of the s_w value allows to change the geometric dimensions of the ribbons. The possibility to control the geometric parameters of the Gd ribbons can be significantly increased by use rectangular-shaped nozzles.

4. Conclusion

Gd ribbons were prepared by the melt-spinning technique. Despite of the fact, that rapid quenching technique suggests the possibility of formation of non-equilibrium structures, obtained ribbon samples showed high structural and magnetic uniformity. The value the magnetic entropy change was comparable with the value the magnetic entropy change known for the bulk Gd. Such melt spinning modes were selected, including the use of the crucible scanning on the surface of the copper wheel, which allows to obtain ribbons with the same value of magnetocaloric effect in a relatively wide range of a copper-wheel speed. However, the variation of the copper-wheel speed value allows to change the geometric dimensions of the ribbons. Thus, Gd melt-spun ribbons are a promising working material for magnetic refrigeration devices, including the flexible case.

Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation (project No. 3.6121.2017) and by ELKARTEK ACTIMAT-3 (2018-19) KK-2018/00099 grant of the Basque Country Government.

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